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(54) Title: STAIN-RESISTANT POLYAMIDE COMPOSITION AND FIBERS (57) Abstract An acid dye stain-resistant fiber-forming composition and a masterbatch concentrate containing a compatible carrier is prepared to obtain fibers for which the feedstock is easier to form, allows different levels of stain resistant reagent to be easily added so that the composition can be formulated for optimum stain resistance requirements influenced by the chosen fiber color, easier drying and prevention of the removal of the stain resistant property characteristic of coating with sulfonate-containing materials. The composition and masterbatch concentrate contains a reagent such as a 5-sulfoisophthalic acid (salt), a portion of which associates with free acid dye sites in the polyamide, thereby disabling them from taking up acid dye stains.		

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**"STAIN-RESISTANT POLYAMIDE
COMPOSITION AND FIBERS"**

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to stain-resistant poly-
amide compositions and fibers and articles of manufacture
5 formed therefrom.

Description of the Prior Art

Textile and carpet yarns prepared from polyamide
fibers are subject to staining by a variety of foods,
drinks and many other compositions with which it comes in
10 accidental contact. The uptake of acid dye stains from,
for example, soft drinks, is a particularly vexing problem
for polyamide fibers due to the availability therein of
acid dye sites such as amine end groups and amide linkages.
Several methods have been suggested for enhancing the
15 resistance of polyamide fibers to acid dye stains.

One approach is to apply a so-called "stain
blocker" coating to the surfaces of polyamide fibers to
prevent access to the acid dye sites therein by the acid
dye staining composition. An example of such a method is
20 illustrated by U.S. Patent No. 5,145,487 which discloses
coating the fibers with sulfonated aromatic condensates
(SACs). Similar proposals are suggested in U.S. Patent
Nos. 4,680,212 and 4,780,099.

Another approach is to form the fibers from poly-
25 amides prepared by copolymerizing monomers, some of which
contain sulfonate moieties. Typical of such systems are
those disclosed in U.S. Patent Nos. 3,542,743; 3,846,507;
3,898,200 and 5,108,684.

U.S. Patent No. 4,374,641 relates to pigment
30 concentrates made using sulfonated polymers as carrier
resins including the highly sulfonated polyamides disclosed
in U.S. Patent No. 3,846,507. U.S. Patent No. 5,236,645

represents an improvement on the invention claimed in U.S. Patent No. 4,374,641.

5 Fibers are generally prepared from polyamides by melt-spinning. Sulfonate containing copolymers generally have higher melt viscosities than non-sulfonate containing copolymers for equivalent relative solution viscosities which limits the extent of polymerization which can be achieved in batch autoclave reaction vessels due to the retardation thereby of the rate of polymerization, as well as its hindrance of effective discharge of the polymerized melt from the reactor. In addition, the presence of sulfonates which have surfactant properties promotes excessive foaming during the melt polymerization process resulting in poor agitation of the reaction mixture and non-uniformity of product.

15 Yarns having different depths of color require different levels of stain protection. Thus, light shaded colors show the presence of stains more than darker colors. It would be advantageous, therefore, to be able to provide different levels of stain resistance to polyamides depending upon the ultimate yarn color without having to provide a separate polyamide feedstock for optimum formulation of each color yarn.

20 An additional disadvantage associated with sulfonate containing polyamide copolymers is that they are generally more difficult to dry than sulfonate-free polyamides due to the hygroscopic nature of sulfonate groups.

25 Polyamides that are topically coated to give stain resistance to the fiber, e.g., with SACs, have the disadvantage that the topical coating is removed during use and maintenance. Gradual removal of the coating will also occur during cleaning with water and detergents. Fibers used for carpet applications may be regularly cleaned with alkaline-based cleaning agents. SAC topical coatings are easily removed using these types of cleaning agents. The

topical coating will also be gradually removed during normal wear of the fiber in its chosen application. In addition to their removal during use and maintenance, SACs generally have inferior resistance to light, oxides of nitrogen, and bleach, the latter of which is commonly used for the cleaning of industrial textiles and carpets. Also, the base color of SACs is not colorless and thus may change the shade of the color of the yarn.

It is an object of the present invention to provide a novel and highly advantageous approach for imparting stain resistance to fibers formed from polyamides.

SUMMARY OF THE INVENTION

The above and other objects are realized by the present invention, one embodiment of which comprises an acid dye stain-resistant fiber-forming polyamide composition comprising:

- a. a fiber-forming polyamide; and
- b. a reagent at least a portion of which associates with free acid dye sites in the polyamide, thereby disabling the acid dye sites in fibers formed from the composition from taking up acid dye stains.

Another embodiment of the invention relates to a masterbatch concentrate for addition to a fiber-forming polyamide to form the above-described acid dye stain-resistant fiber-forming polyamide composition, the concentrate comprising a carrier material compatible with the fiber-forming polyamide, preferably a polyamide, combined with an amount of the reagent in excess of that desired in the acid dye stain-resistant fiber-forming polyamide such that addition of the concentrate to the compatible fiber-forming polyamide results in the desired level of stain resistance.

An additional embodiment of the invention concerns stain-resistant fibers formed from the above-described polyamide compositions.

5 Further embodiments of the invention comprise articles of manufacture prepared with fibers according to the invention such as textiles and carpets.

10 A final embodiment of the invention relates to a method of forming acid dye stain-resistant fibers comprising forming a polyamide composition according to the present invention into fibers by, for example, melt spinning.

DETAILED DESCRIPTION OF THE INVENTION

The terms below have the following meanings herein, unless otherwise noted:

15 "Reagent" refers to any chemical compound, composition or material which associates (as that term is defined below) with the free acid dye sites in a fiber-forming polyamide to thereby render them unavailable for association with an acid dye, which reagent is incapable
20 itself of associating with or taking up the acid dye.

"Association" refers to the chemical reaction or bonding between the reagent and the free acid dye sites in the polyamide which results in prevention of "taking up" of the acid dye by the polyamide, i.e., staining. The association may take the form of a chemical reaction or an
25 acid-salt formulation. Additional types of association include hydrogen bonding, dipole-dipole interaction, Van der Waals forces and coordination complexing.

30 "Acid dye stain" refers to any material or composition which functions as an acid dyestuff by reacting with the free dye sites in polyamides to substantially permanently color or stain the latter.

The term "acid dye sites" refers to those basic sites in polyamides (e.g., amine end groups, amide linkages, etc.) which react or associate with acid dyes, thereby resulting in a stain bonded thereto.

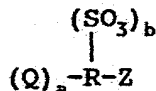
5 "Disabling" the acid dye sites from taking up acid dye stains refers to the effect of the association between the reagent and the acid dye sites which renders the latter less capable of associating with acid dyes such as, for example, those in soft drinks, tomato-based
10 products, etc., which result in staining.

The present invention is predicated on the discovery that optimum levels of resistance to acid dye stain may be imparted to polyamide fibers by compounding certain reagents with fiber-forming polyamide compositions subsequent to polymerization of the polyamide and prior to the
15 formation of the fibers. The invention thereby enables avoidance of the above-enumerated disadvantages associated with coating the polyamide fibers with stain resistant SACs and with formation of the polyamides by copolymerizing sulfonate containing monomers.
20

The selection of a suitable non-acid dyeable reagent having at least one functional group capable of associating with the acid dye sites available in fiber-forming polyamides, thereby rendering those dye sites
25 unavailable for association with acid dye stains, enables the formation of stain-resistant fibers having predetermined and optimum levels of stain resistance not obtainable by the methods and systems of the prior art.

Suitable such reagents include those having at least one functional moiety which preferentially associates
30 with the active acid dye sites in the fiber-forming polyamide and, additionally, contains at least one sulfonyl group. The reagent, of course, should be otherwise substantially inert with respect to the fiber-forming properties of the polyamide.
35

Exemplary of such reagents are those having the formula:



wherein: Q and Z are moieties which associate with the acid dye sites in the polyamide;

a is an integer from 0 to 2;

b is an integer from 1 to 4; and

R is aliphatic, aromatic or alicyclic.

The reagent is selected so as to preferentially associate with the amine end group and/or amide linkage acid dye sites in the polyamide. Preferably, a substantially colorless reagent is selected unless, of course, the reagent is expected to contribute a desired color to the fibers prepared from the polyamide.

The associative functional moieties, Q and Z, may comprise any chemistry that will associate with amine or amide linkages, providing that the functionality does not promote increased stain uptake or otherwise deleteriously impact on the ultimate polyamide composition or articles manufactured therefrom. Thus, Q and Z are preferably combined to form carboxylic anhydride groups or are, individually, carboxylic acid groups or alkali metal, alkaline earth metal or transition metal salts thereof; isocyanate groups; epoxy groups; ester groups and α, β diketone groups. Thio functionalities are generally not employed due to their promotion of yellowing in fibers prepared from polyamide compositions containing them when subjected to light, heat, oxides of nitrogen, etc.

The backbone of the reagent or R may be any suitable aliphatic, aromatic, alicyclic or heterocyclic structure such as phenyl, naphthyl, alkyl (straight or branched chain), cycloalkyl including substituted cycloalkyls, aralkyl, alkenyl and cycloalkenyl.

Exemplary of such reagents are 5-sulfoisophthalic acid, 3-sulfobenzoic acid, 4-(acetoacetamido)benzene sulfonic acid, 4-isocyanatobenzene sulfonic acid, 4-(2,3-epoxypropyl)benzene sulfonic acid, dimethyl-5-sulfoisophthalate, 3,5-di-(2,3-epoxypropyl)benzene sulfonic acid, 3,5-di-isocyanatobenzene sulfonic acid, 3,5-di-(acetoacetamido)benzene sulfonic acid, the sodium and lithium salts of all of the above, and sodium or lithium salt of sulfophthalic anhydride.

The invention is applicable to provide acid dye stain resistance in any fiber-forming polyamide such as nylon-6, nylon-66, MXD-6, nylon-11, nylon-12, nylon-69, the amorphous polyamides such as the copolymer of terephthalic acid and trimethylhexamethylene diamine. Other suitable amorphous polyamides include nylon-6,I (a copolymer of hexamethylene diamine and isophthalic acid), terpolymer of lauryllactam, isophthalic acid and bis(4-amino-3-methylcyclohexyl)methane and polynorbornamide.

The composition may include any of the conventional adjuvants for enhancing the formation of fibers from the polyamide composition such as anti-oxidants, stabilizers, colorants, processing aids, anti-static agents, flame retardants, fillers, nucleating agents, anti-microbials, melt viscosity enhancers or mixtures thereof. Catalysts and/or reducing agents can be added to enhance the association of the reagent with the fiber-forming polyamide. Examples of suitable catalysts/reducing agents include salts of hypophosphites such as sodium hypophosphite, ammonium hypophosphite and manganese hypophosphite, or other phosphorus-containing organic compounds such as phenylphosphinic acid, polyphosphoric acids and triphenyl phosphite.

The compositions are prepared by combining the reagent(s), polyamide(s) and, optionally, adjuvant(s) under conditions which ensure association between the functional

moieties of the reagent and the free acid dye sites in the polyamide(s). Preferably, the polyamide(s) and reagent(s) are combined by melt blending at temperatures above the melting point of the polyamide(s), but below the decomposition temperature of the reagent(s). The reagent(s) and polyamide(s) may be combined in a pre-fiber spinning compounding operation or directly in the fiber melt spinning stage. Product fibers made according to the invention show durable stain-resistant properties equivalent or superior to those produced according to the prior art methods without the consequent disadvantages attendant thereto.

The reagents (and adjuvants, if any) may be combined with the polyamide(s) in any suitable form such as powdered, pelletized, encapsulated, etc. The polyamide(s) may be employed as powder, granules or pellets. The reagent(s) and adjuvant(s) are preferably combined with the polyamide(s) employing a melt extruder and, most preferably, a screw-type extruder. Optimally, a twin-screw extruder of the fully intermeshing type with both screws rotating in the same direction (co-rotating) is employed, although other types of twin-screw extruders may be used such as counter-rotating and/or non-intermeshing types. Single screw extruders may also be successfully employed. The extruder preferably has a barrel length to screw diameter ratio of about 24:1; however, it will be understood that any suitable ratio may be employed depending upon the parameters of the particular compounding process contemplated.

While it is in no way intended to limit the invention by the soundness or accuracy of any theory set forth to explain the nature of the invention, it is postulated that, during the processing step(s), the stain-resistant reagent at least partially associates with, or reacts with, reactive chemical groups or acid dye sites on the polyamide, such as amine end groups or amide linkages.

Removal of volatiles from the compounding mixture aids this association and/or reaction with the polyamide. This removal of volatiles is achieved preferably by the presence of one or more vents on the extruder barrel, although venting is not a requirement for the process of the invention. When a single vent is used with an extruder of a length to diameter ratio of 24 to 1, the vent port is suitably located approximately 19 screw diameters down the length of the barrel. The optimum position of the vent port is determined by the extruder screw profile used. The extraction of volatiles through the vent port is preferably vacuum assisted with a vacuum level of greater than 10 in. Hg and preferably greater than 20 in. Hg. The rate of devolatilization can be assisted through substantially dry nitrogen gas injection through an inlet port located either upstream or downstream of the vent port. Under this situation, a lower vacuum level may be acceptable. Additional ways of promoting the association and/or reaction with the polyamide are through controlled drying of the feedstocks, addition of water-scavenging additives, or a combination of these methods.

The stain-resistant additives and the polyamide resin are preferably fed to the extruder in a pre-dried form with a controlled moisture level. The moisture levels of both the additive and the resin are less than 3,000 ppm and are preferably less than 500 ppm. When drying both of these materials, an inert gas drying atmosphere is preferred. The reagent and the resin may be either fed to the extruder as a blend of the two materials using a single feed hopper or by using separate feed hoppers of a suitable type such as gravimetric or volumetric feeders. Additives to enhance the relative viscosity (RV) of the concentrate can also be added at this stage. When a blend of the materials is used, a double cone tumbler blender is

preferred for preparation of the blend, although other types of blenders may be used.

5 The extruder temperature profiles used and the desired melt temperature during the mixing process will depend, as noted above, principally on the polyamide type and grade chosen. For example, when PA6 is utilized, the melt temperature preferred is between 240°C and 260°C and for PA66 the preferred melt temperature range is between 265°C and 285°C. The optimum melt temperatures for these
10 two resin types will depend on the grade employed.

A preferred embodiment of the invention relates to the preparation of a masterbatch concentrate of polyamide and reagent which can be blended with a suitable fiber-forming polyamide prior to or at the melt-spinning stage to achieve the desired level of stain resistance.
15

Only a small proportion of the reagent is reacted with the polyamide of the concentrate. The bulk of the reagent is dispersed/associated with the resin. It is desired that a proportion of the unreacted reagent in the concentrate becomes reacted/associated with the fiber-forming polyamide. Nylon copolymers are conventionally produced via condensation polymerization where water (or other small volatile molecule, depending on the chemistry) is generated as a by-product. In order to drive this
20 equilibrium reaction forward, it is necessary to remove this water by-product from the system below the equilibrium water concentration. If this is achieved in the fiber spinning line, then association/reaction of the unreacted reagent in the concentrate with the fiber-forming polyamide will occur. In a conventional fiber spinning line, a non-vented extruder barrel is typically used, although vented
25 extruders may be used. The water concentration can be reduced to below the equilibrium value by any of the methods discussed hereinabove.
30

The masterbatch concentrate may be prepared according to the methods described above employing levels of reagent up to about 50% by weight based on the weight of the polyamide.

Any suitable carrier compatible with the fiber-forming polyamide may be employed to prepare the masterbatch concentrate. Although it is preferred to utilize a polyamide carrier, it will be understood that any suitable polymer, polymer blend or other carrier material which is compatible with the fiber-forming polyamide may be employed. Suitable other carriers include polyesters and modified polyolefins. The polyamide used to prepare the masterbatch concentrate may be the same or different in chemical composition from that of the fiber-forming polyamide with which the concentrate is combined to produce the ultimate composition from which fibers according to the invention are formed.

When a stain-resistant concentrate or masterbatch is produced, the melt emerging from the die of the compounding extruder is stranded through a water bath to solidify the melt, followed by air drying of the strand to remove the bulk of the surface water, and pelletization. The concentrate pellets formed are then dried prior to fiber melt spinning to a moisture level of less than 3,000 ppm and preferably less than 500 ppm. This drying of the concentrate is preferably accomplished in an inert gas atmosphere. The concentrate is then mixed on the fiber melt spinning line with non-stain resistant polyamide resin feedstock, dried to a moisture level of less than 3,000 ppm and preferably less than 500 ppm, in the desired ratio depending on the level of stain resistance required in the fiber product. The fiber melt spinning process of a conventional type is used, familiar to those skilled in the art. Other additives such as colorants and stabilizers may be added during the fiber formation process.

The polyamide resin should have a relative solution viscosity of equal to or greater than 2.4 and preferably equal to or greater than 2.7. The relative viscosity of the resin is determined by first preparing 0.55% w/w solutions of the pre-dried polyamide in concentrated sulfuric acid (analytical grade, $96 \pm 0.5\%$). Solution flow times are determined in a Cannon-Ubbelohde size 2 viscometer suspended in a viscometer water bath controlled at $25^\circ\text{C} \pm 0.02^\circ\text{C}$. The flow times of the sulfuric acid are also measured. The relative viscosity is calculated by dividing the flow time of sample solution by the flow time of the solvent. The polyamide resin should also have an amine end group (AEG) level of less than 60 equivalents per 10^6 g and preferably less than 45 equivalents per 10^6 g. The AEG level is determined by means of a potentiometric titration. A known weight of sample is dissolved in m-cresol and titrated against 0.1 M perchloric acid in methanol. A blank titration is also carried out on the m-cresol and used to correct the sample titre.

In the following examples, a standard test is used to evaluate the stain resistance of the yarn formed. It involves the use of an acidified solution of FD&C Red 40 dye which is present in the soft drink cherry-flavored Kool-Aid® commercially sold by Kraft General Foods, Inc.

Typically, $0.1000 \text{ g} \pm 0.0030 \text{ g}$ of FD&C Red 40 dye (CI Food Red 17) is dissolved in $1,000 \text{ cm}^3$ of distilled water. The pH of the dye solution is adjusted to between 2.80 and 2.90 by making small additions of citric acid of technical grade or better. The pH adjusted solution is allowed to reach room temperature, i.e., $21^\circ\text{C} \pm 1^\circ\text{C}$, prior to use.

$1.0000 \pm 0.0010 \text{ g}$ of yarn is placed in 50 cm^3 of the Red 40 solution in a 100 cm^3 glass beaker and the yarn is briefly stirred in the solution to ensure that it is

fully wetted by the solution. The beaker is allowed to stand for 60 minutes without any further agitation.

The yarn is washed for 120 seconds under free-flowing hot tap water, that is at a temperature of 40-50°C. The yarn is then dried by initially blotting with a clean white paper towel to remove the bulk of the surface moisture, followed by allowing it to sit at room temperature for at least 16 hours.

The stain resistance of the yarn is determined by visual comparison to the AATCC Red 40 Stain Scale, which is available from the American Association of Textile Chemists and Colorists (AATCC), Research Triangle Park, North Carolina. The scale consists of ten film squares colored with gradually increasing strengths of FD&C Red 40 numbered from 1 to 10, with 1 being the strongest color and 10 being colorless. The unstained yarn is placed underneath the colored portions of the scale and the stained yarn is placed underneath the colorless portion of the scale and viewed under daylight or equivalent illuminant. The light should be incident upon the surfaces at an angle of $45^\circ \pm 5^\circ$ and the viewing direction should be $90^\circ \pm 5^\circ$ to the plane of the surfaces. The stained yarn is compared to the unstained yarn placed under the closest numbered colored square of the stain scale so that the best color match is obtained. If the color of the stained yarn falls between two squares on the scale, then half grades are used. The number of this colored square, or squares if the match falls between two squares, is called the Stain Rating.

The invention is illustrated by the following non-limiting examples.

EXAMPLE 1

A PA66 resin, polymerized from the salt of adipic acid and hexamethylene diamine, with an RV = 2.7 and an AEG of 40 equivalents per 10^6 g was dried to a moisture level of

less than 500 ppm and tumble blended with 1.5 wt. % of the lithium salt of 5-sulfoisophthalic acid (LiSIPA), also dried to a moisture level of less than 500 ppm. The dry blend was compounded in a vacuum vented 40 mm twin-screw extruder with a length-to-diameter ratio of 24:1. The screw speed was 249 rpm at a throughput rate of approximately 50 kg per hour. The melt temperature of the compound immediately prior to the melt exiting the extruder was measured at 269°C. The vacuum level, as measured directly above the vent of the extruder, was 22 in. Hg. The pelletized product produced was dried to between 400 and 500 ppm before melt spinning into a fiber of 1,850 denier with a filament count of 22 with a trilobal filament cross-section. The undrawn fiber produced was mechanically crimped at a 3.2 draw ratio to give a textured yarn. The stain rating of the yarn using the standard stain test described above was 5.5. The RV of the yarn was 2.54 with an AEG level of 21 equivalents per 10^6 g.

EXAMPLE 2

A PA66 resin with an RV of 3.2 and an AEG level of 27 equivalents per 10^6 g was compounded with 1.5 wt. % of LiSIPA, both dried to similar levels and compounded under similar extrusion conditions as in Example 1 above. The measured melt temperature was 274°C and the vent vacuum level was 23 in. Hg. The compound was dried, spun and textured to give a yarn as per Example 1. The stain rating of the textured yarn using the standard stain test described above was 8.5. The RV of the yarn was 2.50 with an AEG level of 6 equivalents per 10^6 g.

EXAMPLE 3

A similar PA66 resin to that described in Example 1, also with an RV = 2.7, was tumble blended with 10 wt. % of the sodium salt of 5-sulfoisophthalic acid (NaSIPA).

5 The PA66 resin was pre-dried to a moisture level of 380 ppm and the NaSIPA was pre-dried to a moisture level of less than 300 ppm. Using the same extruder and similar extrusion conditions, the dry blend was compounded to give a pellet concentrate. The melt temperature was 269°C and the vent vacuum level was 24 in. Hg. The concentrate was dried to a moisture level of 560 ppm and was blended with the same PA66 resin used to make the concentrate in a 15/85 ratio that was dried to a moisture level of less than 700 ppm. The dry blend was melt spun and textured in a manner similar to Example 1. The textured yarn produced had a stain rating of 5, a yarn tenacity of 2.9 g per denier and a % peak elongation of 37%.

EXAMPLE 4

15 A similar PA66 resin to that described in Example 1, but with an RV = 3.2, was tumble blended with 3 wt. % of LiSIPA. The polyamide resin had been pre-compounded with copper, iodine and phosphorus containing compounds with 35 ppm copper, 1,200 ppm iodine and 100 ppm phosphorus. The polyamide resin had been pre-dried to a moisture level of less than 700 ppm. The LiSIPA was used in its undried form and had a moisture level of 7.0%. The PA66/LiSIPA blend was not pre-compounded prior to introduction to the fiber spinning line. The blend was produced into a textured yarn in a manner similar to Example 1. The textured yarn had a stain rating of 8 with a yarn tenacity of 3.4 g per denier and a % peak elongation of 48%.

EXAMPLE 5

30 A PA6 resin, polymerized from ϵ -caprolactam without chain termination, with an RV = 2.7 and an AEG level of 35 equivalents per 10^6 g, was dried to a moisture level of 650 ppm. The resin was tumble blended with 3% of undried LiSIPA. The PA6/LiSIPA blend was compounded on the

same extruder and under similar extrusion conditions to Example 1 to give a pelletized compound. The vent vacuum level during compounding was measured at 16 in. Hg with a melt temperature of 252°C. The compound was dried to a moisture level of less than 1,000 ppm to produce a textured yarn in a manner similar to Example 1 using process conditions suitable for PA6 that are familiar to those skilled in the art. The stain rating of the textured yarn produced was 6.

EXAMPLE 6

A PA6 resin, similar to that used in Example 5 but with an RV = 3.3 and an AEG level of 27 equivalents per 10^6 g, was pre-dried to a moisture level of 600 ppm. The resin was tumble blended with 3% of undried LiSIPA and 1% of undried sodium hypophosphite. The blend was compounded as per Example 1 with a measured vacuum vent level of 14 in. Hg and a melt temperature of 253°C. The compound was dried to a moisture level of less than 1,000 ppm prior to producing a textured yarn in a manner similar to Example 5. The stain rating of the textured yarn produced was 8.

EXAMPLE 7

A PA66 resin similar to that used in Example 2 was compounded in a similar way to Example 2, except that no venting was conducted during the extrusion step. Poor strandability of the extruded compound was experienced. The compound was dried, spun and textured to give a yarn as per Example 1. The stain rating of the textured yarn using the standard stain test described above was 5.5 with an RV of 2.70.

EXAMPLE 8

A PA66 resin similar to that used in Example 1, but with an AEG level of 57 equivalents per 10^6 g, was

processed as described in Example 1. The stain rating of the textured yarn using the standard stain test described above was 4 with an RV of 2.77.

The feed yarn for manufacture of synthetic textiles and carpets normally takes one of two forms: staple or continuous filament. Staple yarn is produced by spinning an undrawn yarn tow (a large bundle of filaments), that is drawn, mechanically crimped (textured), heat-set and cut into set lengths. The cut yarn is then carded followed by drafting to give a continuous staple yarn. Continuous filament yarn is spun and textured either as a single process or as a multi-step process. The filament bundle size for continuous filament yarn is often considerably smaller than that used for staple tow. The melt spinning portion for both staple and continuous filament yarn types is similar, i.e., molten resin with any desired adjuvants is compounded and fed by a screw extruder or other suitable melting device to a gear pump that forces the melt in a controlled and uniform manner through a melt filtration system and the fine capillaries in a spinneret, followed by air cooling to driven rolls to carry the fibers away from the face of the spinneret. The melting device used should be designed such that satisfactory mixing is achieved to present a substantially uniform melt to the gear pump/spinneret. The actual design will depend on the resin type and grade used and the nature of any adjuvants used. The cross-section of the capillaries in the spinneret is specifically designed for the fiber end use application and will influence the cross-section shape of the spun fiber. Typical shapes are round, deltoid and trilobal. Various types of texturing processes exist for crimping continuous filament including a stuffer-box, air-jet and false-twist texturing. Drawing of the yarn is typically a precursor of the texturing process.

There are typically three types of methods for forming fibers into apparel, textiles and carpets: (1) weaving, (2) knitting, including warp and circular types, and (3) non-woven techniques, including tufting.

5 Woven fabrics consist of sets of yarns interlaced at right angles in established sequences on a loom. Knitting consists of forming loops of yarn with the aid of thin, pointed needles or shafts. As new loops are formed, they are drawn through those previously shaped. This inter-
10 looping and the continued formation of new loops produce knit fabrics. Non-woven fabrics consist of a web of staple or filament fibers held together either by application of a bonding or adhesive agent or by the fusing of fibers by application of heat. Tufting consists of inserting loops
15 into an already formed backing fabric. The backing fabric may be of any type and composed of any fiber, including both natural and synthetic fibers such as jute and polypropylene. The yarn loops are inserted into the backing with needles. The loops can be cut or left uncut. They are
20 held in place either by applying a special coating or by untwisting the tufted yarn and shrinking the backing fabric.

Fibers of the present invention may be combined
25 into yarn according to methods and systems well known to those skilled in the art. Either the fibers or yarns prepared therefrom may be manufactured into novel textiles, carpets and other articles of manufacture requiring polyamides having enhanced resistance to staining by acid dyestuffs according to conventional, well known methods.

**"STAIN-RESISTANT POLYAMIDE
COMPOSITION AND FIBERS"**

I CLAIM:

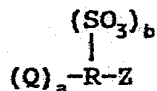
1 1. An acid dye stain-resistant fiber-forming
2 polyamide composition comprising:

- 3 a. a fiber-forming polyamide; and
4 b. a reagent at least a portion of which
5 associates with free acid dye sites in said polyamide,
6 thereby disabling said acid dye sites in fibers formed from
7 said composition from taking up acid dye stains.

1 2. The composition of claim 1 wherein said
2 reagent associates with acid dye sites comprising amine
3 groups and/or amide linkages in said polyamide.

1 3. The composition of claim 1 wherein said
2 reagent is substantially colorless.

1 4. The composition of claim 1, said reagent
2 having the formula:



4 wherein: Q and Z are moieties which associate with said
5 acid dye sites in said polyamide;

6 a is an integer from 0 to 2;

7 b is an integer from 1 to 4; and

8 R is aliphatic, aromatic or alicyclic.

1 5. The composition of claim 4 wherein at least
2 one of said Q and Z is a carboxylic acid group or a salt
3 thereof.

1 6. The composition of claim 4 wherein at least
2 one of said Q and Z is an isocyanate group.

1 7. The composition of claim 4 wherein at least
2 two of said Q and Z combine to form a carboxylic acid
3 anhydride.

1 8. The composition of claim 4 wherein said
2 reagent is 5-sulfoisophthalic acid or a salt thereof.

1 9. The composition of claim 8 wherein said
2 reagent is an alkali metal, alkaline earth metal or transi-
3 tion metal salt of 5-sulfoisophthalic acid.

1 10. The composition of claim 9 wherein said
2 reagent is the lithium salt of 5-sulfoisophthalic acid.

1 11. The composition of claim 9 wherein said
2 reagent is the sodium salt of 5-sulfoisophthalic acid.

1 12. The composition of claim 4 wherein said
2 reagent is 3-sulfobenzoic acid or the sodium or lithium
3 salt thereof.

1 13. The composition of claim 1 wherein said
2 fiber-forming polyamide is nylon-6.

1 14. The composition of claim 1 wherein said
2 fiber-forming polyamide is nylon-66.

1 15. The composition of claim 1 wherein said
2 fiber-forming polyamide is MXD-6.

1 16. The composition of claim 1 wherein said
2 fiber-forming polyamide is nylon-11.

1 17. The composition of claim 1 wherein said
2 fiber-forming polyamide is nylon-12.

1 18. The composition of claim 1 wherein said
2 fiber-forming polyamide is nylon-69.

1 19. The composition of claim 1 wherein said
2 fiber-forming polyamide is an amorphous polyamide.

1 20. The composition of claim 19 wherein said
2 fiber-forming amorphous polyamide is a copolymer of tereph-
3 thalic acid and trimethylhexamethylene diamine.

1 21. The composition of claim 1 additionally
2 containing a fiber-forming adjuvant.

1 22. The composition of claim 21 wherein said
2 fiber-forming adjuvant is an anti-oxidant, stabilizer,
3 colorant, processing aid, catalyst, filler, nucleating
4 agent, anti-microbial, melt viscosity enhancer or mixtures
5 thereof.

1 23. The composition of claim 1 formed by melt
2 blending said reagent and said fiber-forming polyamide.

1 24. A masterbatch concentrate for addition to a
2 fiber-forming polyamide to form the acid dye stain-
3 resistant fiber-forming polyamide composition of claim 1
4 comprising a carrier compatible with said fiber-forming
5 polyamide combined with an amount of said reagent of claim
6 1 in excess of that desired in said acid dye stain-
7 resistant fiber-forming polyamide.

1 25. The masterbatch concentrate of claim 24
2 wherein said carrier is a polyamide.

1 26. The masterbatch concentrate of claim 25
2 wherein said polyamide is identical in chemical composition
3 to said fiber-forming polyamide.

1 27. The masterbatch concentrate of claim 25
2 wherein said polyamide is different in chemical composition
3 from said fiber-forming polyamide.

1 28. An acid dye stain-resistant fiber-forming
2 composition comprising a fiber-forming polyamide and the
3 masterbatch concentrate of claim 25.

1 29. The composition of claim 28 formed by melt
2 blending said fiber-forming polyamide and said masterbatch
3 concentrate.

1 30. An acid dye stain-resistant fiber or fibers
2 formed from the composition of claim 1.

1 31. An article of manufacture prepared with the
2 fiber or fibers of claim 30.

1 32. A textile article according to claim 31.

1 33. A carpet according to claim 32.

1 34. A method of forming an acid dye stain-
2 resistant fiber or fibers comprising forming the composi-
3 tion of claim 1 into a fiber or fibers.

1 35. The method of claim 34 comprising melt
2 spinning said composition to form a fiber or fibers.

1 36. A method of forming an acid dye stain-
2 resistant fiber or fibers comprising combining a master-
3 batch concentrate according to claim 25 with a fiber-
4 forming polyamide compatible therewith and forming a fiber
5 or fibers therefrom.

1 37. The method of claim 36 comprising melt
2 spinning said combination of masterbatch concentrate and
3 fiber-forming polyamide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/06126

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B29C 47/00, 47/04, 47/88; C08G 69/14, 69/16
US CL : 264/75, 176.1, 211; 428/364, 365; 525/420, 432

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/75, 176.1, 211; 428/364, 365; 525/420, 432

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, JPOABS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,340,886 (HOYT ET AL.) 23 August 1994, column 3, lines 33-36 and column 4, lines 44-54.	1-8, 13, 14, 16, 17, 23, 30, 34, 35
X	WPAT ACCESSION NO. 94-303668/38 (SANDOZ PATENT GMBH) 29 September 1994, see entire document).	1-8, 13, 14, 16, 17, 23, 30, 34, 35
X	US, A, 4,391,968 (MERANI ET AL.) 05 July 1983, column 1, lines 43-66 and column 4, table.	1-10, 23, 30, 34, 35
Y	US, A, 5,236,645 (JONES) 17 August 1993, column 2, lines 64-67; column 3, lines 8-12 and column 4, lines 17-19.	1-11, 13-23, 30, 34, 35
Y	US, A, 5,164,261 (WINDLEY) 17 November 1992, column 3, lines 1-3.	1-11, 13-23, 30, 34, 35

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Special categories of cited documents:		Enter document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"T"	
"E" earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed	"Z"	document member of the same patent family

Date of the actual completion of the international search: 01 AUGUST 1996	Date of mailing of the international search report: 19 AUG 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20251	Authorized officer: ROBERT SELLERS
Facsimile No. (703) 305-3250	Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/06126

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,108,684 (ANTON ET AL.) 28 April 1992, column 2, lines 47-55.	1-11, 13-23, 30, 34, 35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/06126

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-11, 13-23, 30, 34, 35

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/06126

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- I. Claims 1-23, 30, 34 and 35, drawn to a polyamide composition, fibers formed therefrom, and a method of forming fibers, classified in class 525, subclass 420.
- II. Claims 1-23, 31 and 32, drawn to a polyamide composition and a textile article formed therefrom, classified in class 139, subclass 420A.
- III. Claims 1-23, 31 and 33, drawn to a polyamide composition and a carpet formed therefrom, classified in class 428, subclass 225.
- IV. Claims 24-27, drawn to a masterbatch concentrate comprising a carrier and reagent, classified in class 525, subclass 323.
- V. Claims 28, 29, 36 and 37, drawn to a composition comprising a polyamide and a master batch concentrate, classified in class 525, subclass 432.

The inventions of Groups I-V do not meet the criteria for unity of invention as required by PCT Rule 13.2 for the following reasons:

Inventions I, II and III lack unity of invention because the fibers of Invention I (claim 30), the textile of Invention II (claim 32) and the carpet of Invention III (claim 33) are three distinct uses of the polyamide composition based on the structural differences between a fiber, a textile and a carpet.

Inventions I, II and III lack unity of invention from Invention IV since the polyamide of Inventions I, II and III and the carrier of Invention IV are physically diverse due to the pelletized form of the polyamide and the liquid form of the carrier.

Inventions I, II, III and IV lack unity of invention from Invention V because the chemical structure of final product of Group V prepared from the intermediates of Invention I, II, III and IV is unknown. There is no evidence that the characteristic of the final product which is the inventive feature is due to the intermediate.

The reagents of claims 8-11 and claim 12 do not possess chemical structures considered to be technically closely interrelated and are not recognized as a single class of compounds based on the different quantitative acid functionalities of the reagents which react with the acid dye sites of the polyamide to yield distinct final product structures.